

SYNTHESIS OF PIGMENTS BASED ON THE CALCIUM-SILICATE SYSTEM

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The results of studies of the synthesis of brightly-colored lilac and light-green pigments in the system CaO – SiO₂ with the addition of chromophores and modifiers are presented. X-ray phase analysis and IR spectroscopy established the process resulting in the formation of the structure of the pigment and the optimal synthesis temperature. The results of tests of the pigments in glaze melts are indicated.

Key words: pigments, chromophore, color, spinel, silicates.

An important problem in the modern production of porcelain-earthenware articles is expanding the assortment and increasing their quality by using new coloring coatings. To this end, it is necessary to develop new compositions of ceramic pigments that do not contain expensive raw-materials such as ZrO₂, Sb₂O₃, SnO, PbO, and others. Accessible inexpensive components are chalk, quartz sand, and oxides of transition metals — chromium, cobalt, iron, nickel, and others. The production of ceramic pigments is an energy-intensive process, so that it is important to develop new compositions with lower synthesis temperatures.

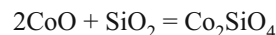
The result of studies of two compositions of ceramic pigments with bright lilac and bright light-green colors in the system CaO – SiO₂ are presented in this work. It is well-known [1, 2] that, according to the phase diagram, when their ratio changes the initial oxides can form nonrefractory calcium metasilicates in three modifications — wollastonite (low-temperature form), parawollastonite and pseudowollastonite (high-temperature), which are synthesized at temperatures above 1100°C. Alkaline-earth metal oxides as well as ZnO and BaO, which have a positive effect on the color of a pigment and lower the synthesis temperature, were used as modifying agents to intensify the chromophoric properties of the pigments. Since calcium metasilicate is formed with CaO and SiO₂ ratio 1 : 1, SiO₂ was also added to ensure the formation of the color-carrying phase represented by transition-metal orthosilicates. It was determined that for CaO : SiO₂ = 1 : 2 a bright lilac-colored pigment is formed when cobalt and zinc oxides are introduced. A pigment with a bright light-green color was synthesized by adding Cr₂O₃ and BaO. The calcination temperature affects the color cha-

acteristics of a pigment. The variation of the color characteristics of pigments as a function of the synthesis temperature is illustrated in Table 1. The color characteristics of the pigments studied were determined with a spectrometer.

Analysis of the data presented in Table 1 established the optimal purity of color tone and the dominant wavelength of the pigments synthesized at different temperatures. To eliminate swelling of the glaze coating with the bright light-green pigment the synthesis temperature of the pigment was raised to 1200°C.

The phase composition of the pigments was investigated in the temperature interval 20 – 1200°C by means of high-quality x-ray phase analysis performed with a DRON-2 spectrometer.

We note that the system CaO – SiO₂ – CoO has still not been adequately studied [3]. A violet colored cobalt silicate is formed according to the reaction



at temperature 1000°C. Cobalt compounds are characterized by a tendency to form tetrahedral and octahedral complexes, which form the spinel Co²⁺Co³⁺O₄.

TABLE 1. Color Characteristics of Pigments

Pigment	Synthesis temperature, °C	Dominant wavelength, nm	Tone purity, %
Bright lilac	700	481.5	8.0
	900	480.0	9.5
	1100	478.0	14.5
Bright light-green	700	574.8	65.0
	900	574.0	50.0
	1200	585.5	39.0

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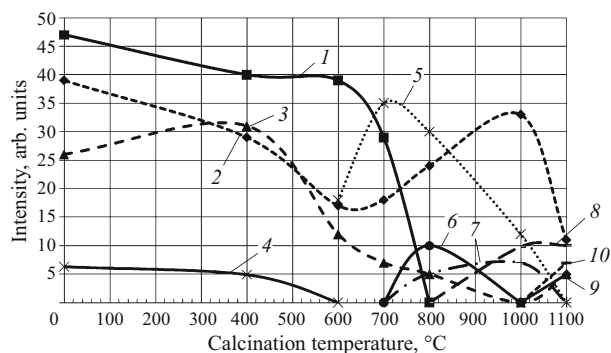


Fig. 1. Intensity of the diffraction peaks of the main crystalline phases as a function of the calcination temperature: 1) CaCO_3 ; 2) SiO_2 ; 3) Co_3O_4 ; 4) ZnO ; 5) ZnCo_2O_4 ; 6) CaO ; 7) CoO ; 8) $\text{Ca}_2\text{CoSi}_2\text{O}_7$; 9) $\text{Ca}_2\text{ZnSi}_2\text{O}_7$; 10) Co_2SiO_4 .

The intensity of the diffraction peaks of the main crystalline phases of the bright-lilac pigment at function of the calcination temperature is presented in Fig. 1. As the data presented show, no large changes in the composition of the initial masses occur in the interval 400–600°C. It was determined with further heating to 1000°C that solid solutions based on spinel of the type $(\text{Co}, \text{Zn})\text{Co}_2\text{O}_4$ are formed. At temperatures 1000–1100°C cobalt and zinc silicates are formed with the compositions Co_2SiO_4 , $\text{Ca}_2\text{CoSi}_2\text{O}_7$, and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$.

With a subsequent increase of temperature the intensity of the main characteristics peaks in the diffraction pattern of Co_2SiO_4 was observed to decrease, which is what leads to a decrease of pigment brightness.

The infrared spectra of the products of calcination of this pigment composition are presented in Fig. 2a. The spectrum

of the sample heated to 700°C contains a characteristic absorption band near 1420 cm^{-1} , which characterizes the vibrations of the carbonate groupings. Thus, CaO was introduced by means of CaCO_3 . Bands in the region $800\text{--}1100\text{ cm}^{-1}$ are characteristic for some Si-O bonds. The deformation vibrations of the Si-O-Si bonds lie in the region $580\text{--}700\text{ cm}^{-1}$. The vibrations of the Me-O bonds characteristic for spinels predetermine the appearance of the band in the region $400\text{--}600\text{ cm}^{-1}$. As temperature increased to 900°C no changes were observed in the absorption bands, but their intensity decreases. The 580 cm^{-1} band is characteristic for zinc in tetrahedral coordination and corresponds to Zn_2SiO_4 . At 1200°C the bands in the interval $800\text{--}1100\text{ cm}^{-1}$ undergo differentiation, which attests to an increase in the degree of polymerization of the silicon-oxygen complexes. Specifically, the formation of diorthosilicates is confirmed by the appearance of a band near $670\text{--}650\text{ cm}^{-1}$ and corresponds to the spectrum of hardystonite $\text{Ca}_2\text{Zn}(\text{Si}_2\text{O}_7)$ [4, 5].

According to electron microscopy, as temperature increases, the crystals grow from $0.025\text{--}0.05\text{ }\mu\text{m}$ to $0.2\text{ }\mu\text{m}$. The crystals decompose at 1200°C.

For the bright light-green pigment containing CaO , SiO_2 , Cr_2O_3 , and BaO , synthesized by soaking at each temperature position for 1 h, in the temperature interval 400–1200°C, the following changes were observed in the phase composition.

At 700°C reflections characteristic for BaCrO_4 and BaCr_2O_4 are observed in the diffraction pattern. Silica and calcium carbonate are also present. The main changes at 800°C are decomposition of CaCO_3 and possibly the formation of CaO-SiO_2 , 2CaO-SiO_2 , and 3CaO-SiO_2 [1]. At 800°C CaSiO_4 and $\text{Ca}_3\text{Si}_2\text{O}_7$ form in the products of calcina-

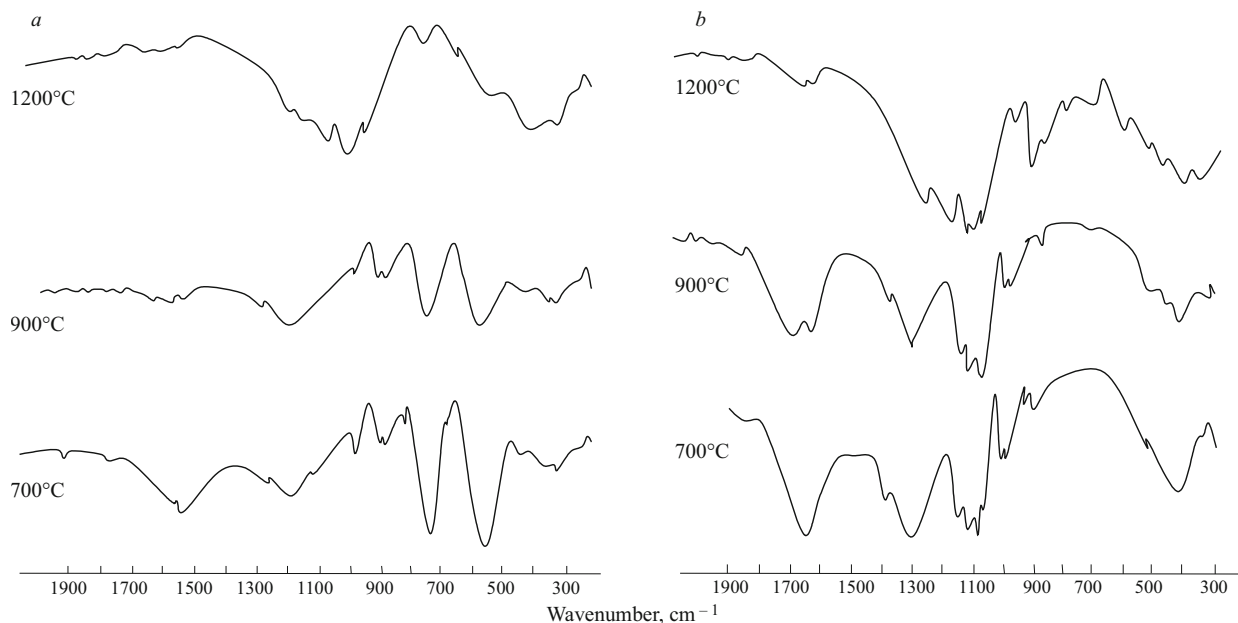


Fig. 2. Curves of the infrared spectra of bright violet (a) and bright light-green (b) pigments.

tion, and the presence of BaCrO_4 and BaCr_2O is also observed.

As temperature increases further to 900°C , the number of crystalline phases of BaCrO_4 and BaCr_2O_4 increases. Calcium orthosilicate undergoes polymorphic transformations in the form of an intermediate form β - and β' - $2\text{CaO} \cdot \text{SiO}_2$. Silica and chromium oxide are present in the calcination products. At 1000°C the phase composition remains practically unchanged with the exception of BaCrO_4 and BaCr_2O_4 , whose amount decreases.

The formation of solid solutions based on Ba_2SiO_4 and Ca_2SiO_4 was observed in the interval $1100 - 1200^\circ\text{C}$ [2]. It was found that the phases $\text{BaO} - 2\text{SiO}_2$, $\text{CaO} - \text{SiO}_2$, SiO_2 , and BaCr_2O_4 form in the ternary system $\text{SiO}_2 - \text{CaO} - \text{BaO}$.

Thus, successive calcination in the temperature indicated made it possible to trace a series of continuous phase and structural transformations, occurring when the pigments are synthesized, as well as to establish the optimal temperature of synthesis.

To confirm the results obtained from the analysis of the XPA data for the bright light-green pigment, infrared absorption spectra are obtained and are presented in Fig. 2b. The absorption bands of the calcined pigments at 700°C 1435 and 875 cm^{-1} can be attributed to calcium carbonates. The absorption maxima at 1080 and 463 cm^{-1} indicate the presence of isolated SiO_4 tetrahedra. As temperature increases to 900°C absorption bands of the orthosilicate Ca_2SiO_4 appear at 823, 860, 935, and 890 cm^{-1} . The absorption bands in the range $400 - 600\text{ cm}^{-1}$ could be due to deformation vibrations of bridge bonds $\text{Si} - \text{O} - \text{Si}$ and vibrations of $\text{Me} - \text{O}$, characteristic for spinel compounds [4]. As temperature increases, the absorption bands of the bridge bonds $\text{Si} - \text{O} - \text{Si}$ in the region $600 - 700\text{ cm}^{-1}$ show appreciable structural

transformations in the pigment, which are due to the formation of groupings of the type SiO_2 . The shift of the absorption peak in the region $900 - 1100\text{ cm}^{-1}$ in the direction of shorter wavelengths indicates an increase of the degree of polymerization of the silicon-oxygen complexes.

The broadening of the absorption bands in the region $450 - 600\text{ cm}^{-1}$ attests to the presence of chromito- and chromatobarium polyanionic complexes.

In summary, it has been confirmed by means of IR spectroscopy that chain silicates form at 1200°C and the maximum amount of spinels is formed. Cubic crystals are found in the electron-microscope photographs. This confirms the optimal synthesis temperature to be 1200°C .

The pigments synthesized were tested as chromophoric components in glaze melts, crude and fritted in the concentration 2.5 – 5%. The results confirmed the stability of glaze coatings with violet and light-green colors.

REFERENCES

1. N. M. Bobkova, *Physical Chemistry of Refractory and Non-Metallic Silicate Materials* [in Russian], Vyssh. Shkola, Moscow (2007).
2. G. N. Maslennikova and I. V. Pishch, *Ceramic Pigments* [in Russian], Stoit. Materialy, Moscow (2009).
3. P. R. Toropov, V. P. Borzakovskii, V. V. Lapin, and N. I. Kurtseva, "Phase diagrams of silicate systems," *Troinye Silikat. Sistemy*, No. 3 (1972).
4. I. Ya. Plyusnina, *Infrared Spectra of Silicates* [in Russian], Stroiizdat, Moscow (1970), pp. 182 – 188.
5. P. I. Buravskii, "Investigation of the structural transformations in petrological melts and glasses by means of infrared spectroscopy," *Vse Problemy Kammenogo Lit'ya*, No. 3, 75 – 93 (1975).